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National HIPIMS Technology Centre UK

Low-Pressure Plasma Nitriding Of Medical Grade Alloy Using HIPIMS Discharge

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1.Introduction:

- CoCrMo is a biomedical grade alloy which is widely used in the manufacturing of orthopaedic implants such as hip and knee replacement joints because it has high hardness, adequate corrosion resistance, and excellent biocompatibility [K. Shukla et al., 2020].
- However, the major concern is the release of toxic metal ions due to corrosion and wear of the alloy, which causes an allergic reaction in the human body. [Öztürk et al., 2006]
- Over the years various surface modification techniques including nitriding have been used to improve the performance of CoCrMo (F75) alloy.
- In the current work the material properties of a surface layer produced by a novel low-pressure plasma nitriding process are described. Unlike state-of-the-art plasma nitriding based on a DC glow discharge,(DCPN) the new process utilises a HIPIMS discharge to further enhance the ionisation of the reactive gas Nitrogen in the vacuum chamber, [P. Hovsepian et. al, 2003].

2. Objectives:

- To improve the mechanical, tribological and corrosion performance of CoCrMo alloy by thermochemical plasma surface modification.
- To enhance the process productivity by utilising highly ionised reactive gas plasma generated by a HIPIMS discharge.
- To compare the material and performance properties of the nitrided layers produced with the new technique to those obtained from layers produced by industry provided nitrided specimen used as a benchmark.

3. Methodology:

- Nitriding System: The experiments have been carried out in a Hauzer HTC 1000-4 PVD system enabled with HIPIMS technology at the National HIPIMS Technology Centre UK at Sheffield Hallam University.
- HIPIMS discharge was sustained on one pair of Nb and Cr targets.
- The nitriding voltage was varied in a vide range, (between -600V and -1000V) for process optimisation.
- The other process parameters such as nitriding time (t) = 4 Hours, Total Pressure (P) = 10^{-3} mbar. and nitriding Temperature (T) = 400ºC were kept constant.
- Industry provided specimen nitrided in a DC glow discharge at nitriding temperature (T) = 400ºC and nitriding voltage of -1000V, for 20 hours was used for comparison.

Abbreviations: APS: as polished substrate, HLPN: HIPIMS low pressure nitriding, DCPN: DC plasma nitriding.

4. Characterisation:

The properties of the nitrided layers were investigated by a vide range of advanced surface analytical techniques.

- SEM, XRD, Nanoindentation, 5 mN (Hp), Vickers diamond indentation, 50 kgf (for fracture toughness K_{Ic}). Pin-on-disc test for tribological characterisation and potentiodynamic polarisation test.
- Fracture toughness characterisation by calculating K_{Ic} value : $K_{IC} = \delta \left(\frac{E}{H}\right)^{0.5} \left(\frac{P}{c^{3/2}}\right)$

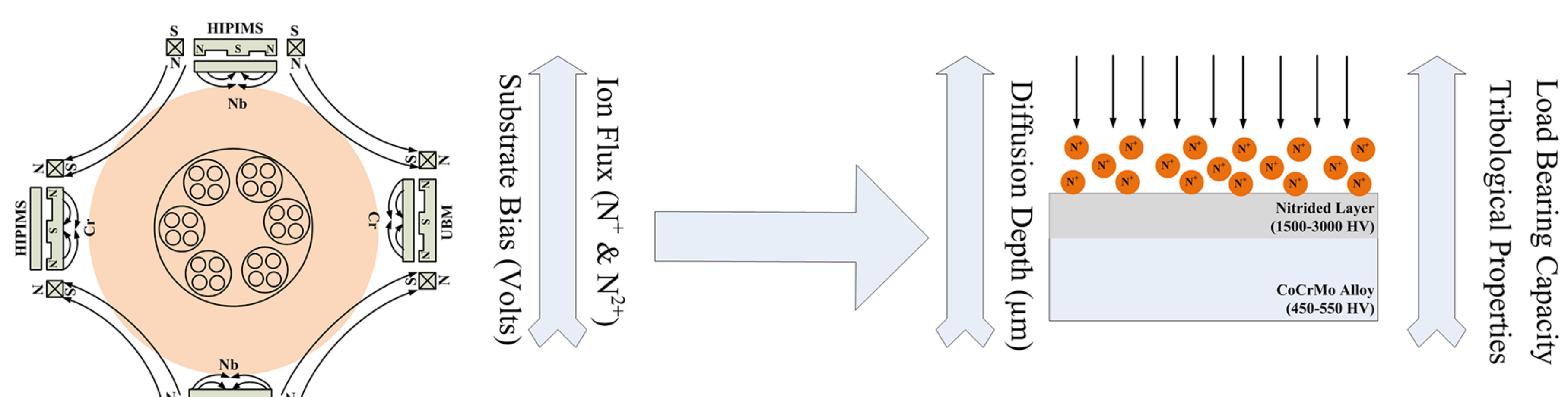

Figure 1. Schematic of Nitriding Setup

5. Results and Discussion:

5.1 Crystallographic structure:

ID	Texture Coefficient, T*%
DC PN	86 [γN(111)]
HL PN	44:56 [γN(111)]

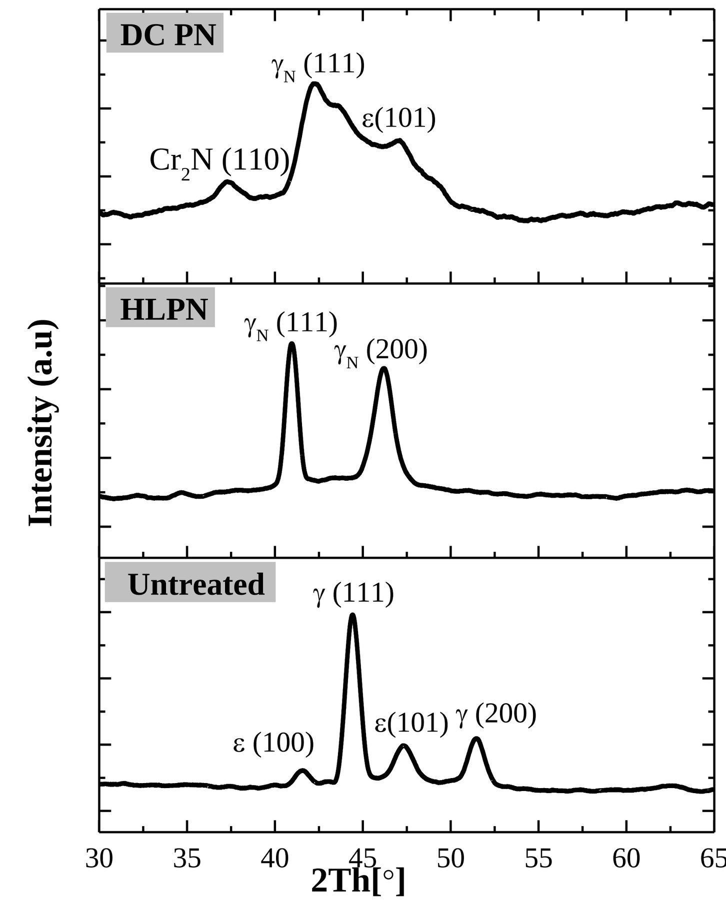

Figure 2: XRD spectra of DC PN and HIPIMS PN. γN(111): FCC structure whereas γN(200): HCP structure.

5.2 Thickness Measurement:

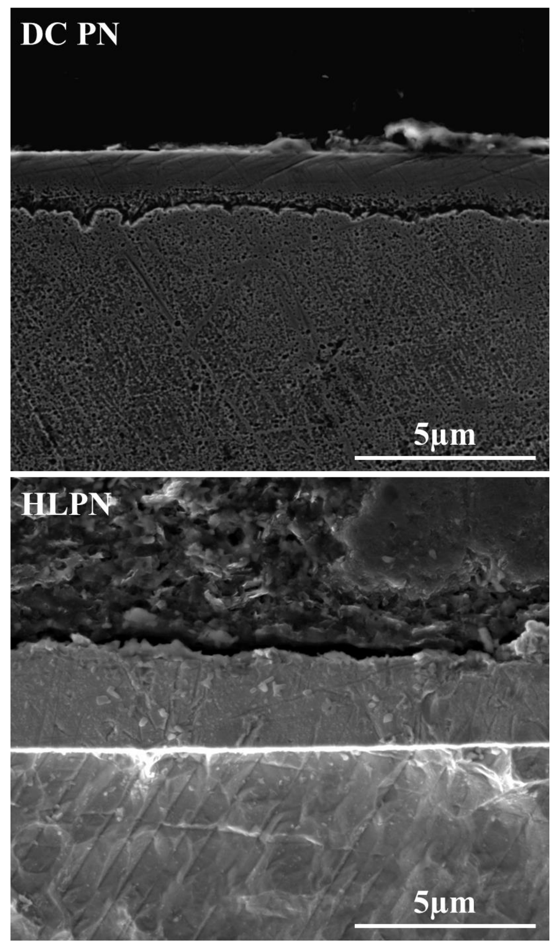

Figure 3: SEM cross-section of DCPN and HLPN. Nitrided layer thickness of 1.43 µm (achieved in 20 hours) and 2.79 µm (achieved in 4 hours) have been measured for the DC PN and HIPIMS PN respectively revealing that the nitriding rate of the HIPIMS PN was factor of 10 higher than that of the DCNP.

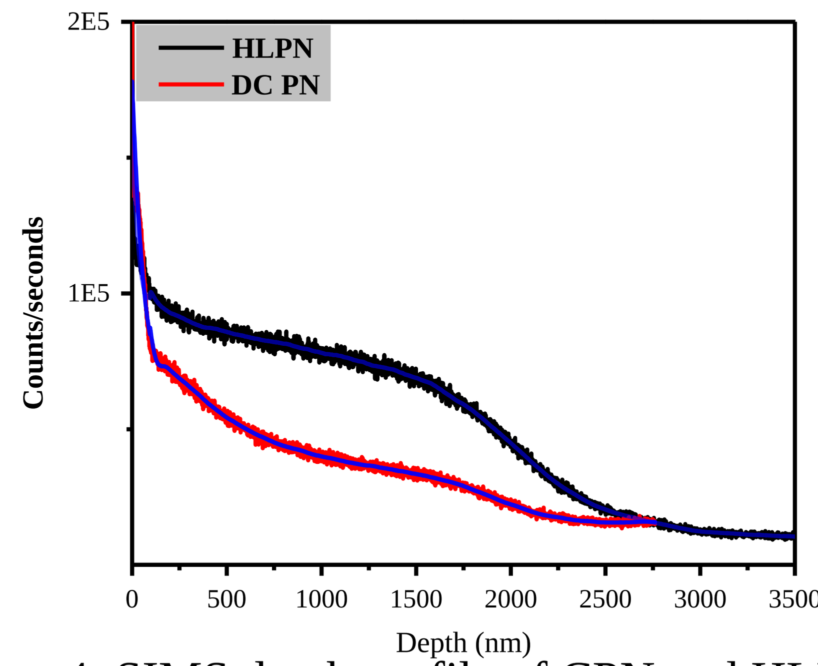

Figure 4: SIMS depth profile of CPN and HLPN Compared to DCPN, HIPIMSPN allows almost factor of two higher nitrogen concentration in the nitrided layer at the control depth of 1.5 µm.

5.3 Mechanical and Tribological Study:

Sr. No.	Hp (GPa)	E (GPa)	μ	Kc ($m^3N^{-1}m^{-1}$)	D_T SIMS (µm)	D_T SEM-CS (µm)	H/E	H^3/E^2	K_{Ic} ($MPamm^{1/2}$)
CoCrMo	8	249	0.8	6.00E^{-14}	-	-	0.04	0.008	908
DC PN	20	276	0.6	2.20E^{-15}	2.1	1.43	0.07	0.105	950
HLPN	23	287	0.62	1.18E^{-15}	2.91	2.79	0.08	0.147	917

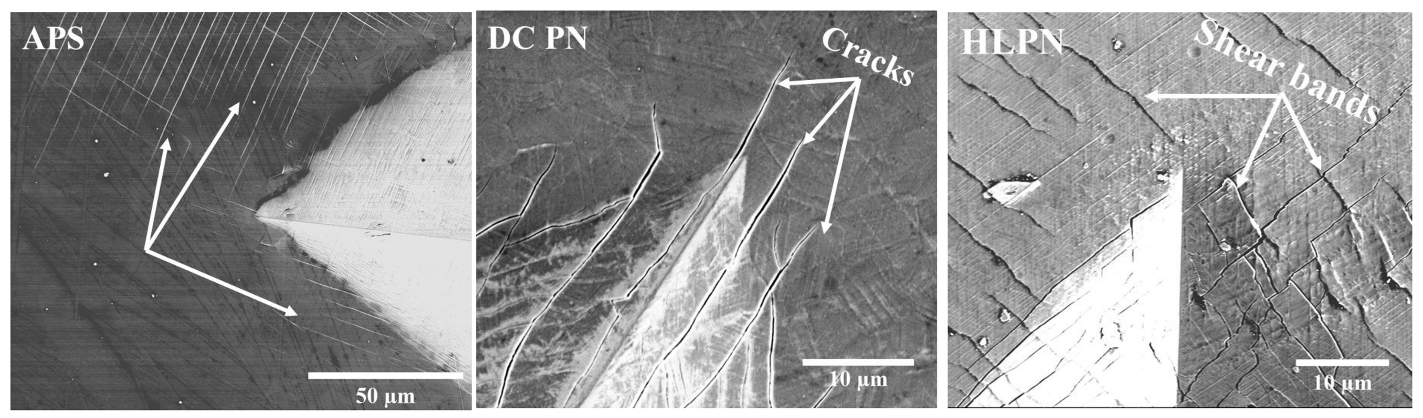

Figure 5: SEM images of the indentation impression in Vickers microhardness test for the untreated and various plasma nitrided alloys . Dense network of cracks observed for the DCPN case. The crack free indentation impression obtained with the HLPN sample demonstrates the high fracture toughness of this nitrided layer.

5.5 Corrosion Test:

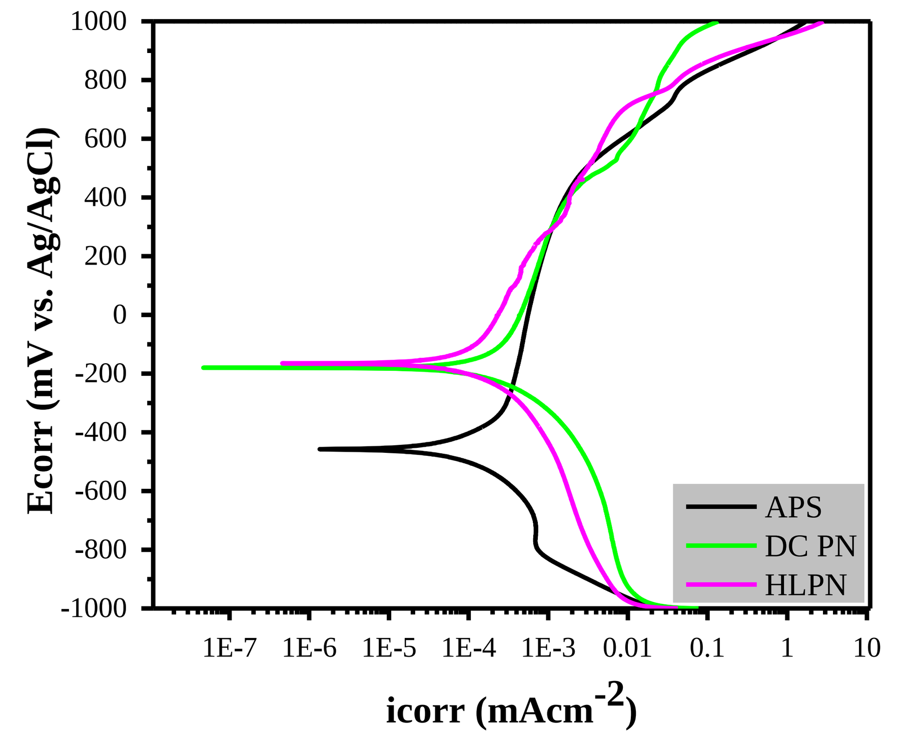

Figure 6: Potentiodynamic polarisation curve of APS, DC PN and HLPN in Hank's solution (pH:7.3).

6. Conclusions:

1. The nitriding rate of HIPIMSPN was found to be factor of 10 faster than that of the benchmark DCPN.
2. Compared to DCPN, HLPN allows almost factor of two higher nitrogen concentration in the nitrided layer at the control depth of 1.5 µm.
3. HLPN produced nitrided layers show higher hardness, (Hp=23 GPa) and higher wear resistance, (wear coefficient Kc=1.18E^{-15} m^3Nm^{-1}) as compared to DCPN process (Hp=21 GPa, Kc=2.20 E^{-15} m^3Nm^{-1}).
4. The high H/E, H3/E2 and K_{Ic} values respectively are indicative for the high fracture of toughness of the nitrided layers produced with the novel HLPN technology.
5. With Higher corrosion potential, Ecorr=-160 mV and higher pitting potential, Up=770 mV the HLPN nitrided layers showed superior corrosion performance in Hank's solution (pH:7.3) when compared to DCPN (Ecorr=-182 mV, Up=400 mV) providing reliable corrosion protection of the untreated CoCrMo (F75) alloy.

7. References:

Arcam EBM system, ASTM F75 Cobalt Chrome Alloy, *2007.*

Öztürk et al., Metal ion release from nitrogen ion implanted CoCrMo orthopaedic implant material, *SAC, 2006.*

P. Hovsepian et. al, Performance of High-Precision Knife Blades Treated by Plasma Nitriding and PVD Coating, *Proceedings, Annual Technical Conference - Society of Vacuum Coaters, 2003.*

8. Acknowledgement:

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